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Photoluminescent and Electroluminescent Properties
of $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$ Electrodes

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PHOTOLUMINESCENT AND ELECTROLUMINESCENT PROPERTIES OF $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$ ELECTRODES

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Quenching of photoluminescence (PL) and initiation of electroluminescence (EL) from n-type $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$ electrodes is used to map the electric field in these solids, grown by a modified Bridgman method.

1. INTRODUCTION

Photoluminescence (PL) and electroluminescence (EL) can be used to characterize electric fields in semiconductor electrodes through their influence on electron-hole (e^-h^+) pair recombination¹. Solid solutions of II-VI compounds such as n-CdS and n-CdSe have provided a useful family of tunable band gap materials for such studies². We have extended these studies to emissive electrodes derived from a solid solution of MnSe and CdSe. In this paper we report that PL from n- $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$ electrodes used in photoelectrochemical cells (PEC's) can be used to map the electric field in these solids, and that EL obtained from the electrodes originates, on average, nearer the semiconductor-electrolyte interface than PL.

2. SYNTHESIS AND CHARACTERIZATION

Single-crystal samples of n- $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$ were grown by a modified Bridgman method³; samples with carrier concentrations, n , ranging from $\sim 10^{16}$ – 10^{18}cm^{-3} (Hall method) were etched with 1:20(v/v) Br_2/MeOH prior to use. When excited with ultraband gap light (E_g 1.75eV⁴), the samples emit with $\lambda_{\text{max}} \sim 694\text{nm}$, Fig.1. The spectral maximum is near E_g and blue-shifts to $\sim 665\text{nm}$ at 77 K; radiative quantum efficiencies, ϕ_r , for the edge emission generally range from $\sim 10^{-5}$ to 10^{-4} .

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3. PL PROPERTIES IN A PEC

When the solid serves as the photoanode of a PEC employing diselenide electrolyte, its PL intensity can be quenched by applied potential. Figure 1 presents photocurrent - PL intensity - voltage data (*iLV curves*) for a $n\text{-Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$ -based PEC; the potential-independent spectral distribution permits PL to be monitored at λ_{max} . Quenching of PL in PEC's has been described using a dead-layer model originally applied to semiconductor-metal, Schottky barrier systems: e^-h^+ pairs formed within a distance on the order of the depletion width do not contribute to PL; this model thus relates PL intensity to the thickness of the electric field in the electrode^{5,6}. The quantitative form of the model is given by eq. (1), where ϕ_r and $\phi_{r\text{FB}}$ are

$$\frac{\phi_r}{\phi_{r\text{FB}}} = \exp(-\alpha'D) \quad (1)$$

radiative efficiencies in circuit and at flat-band potential (assumed to be open circuit), respectively; D is the dead-layer thickness; and $\alpha' = \alpha + \beta$ with α and β the solid's absorptivities for the exciting and emitted light.

Although ultraband gap absorptivities have not been measured for $n\text{-Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$, values of α can be estimated by blue-shifting the CdSe absorption spectrum⁷ by $\sim 25\text{nm}$, since the solids have similar electronic structures. The PL quenching resulting from a given excitation wavelength then leads, in conjunction with the estimated value of α and eq. (1), to a value for D . For the Fig. 1 data, D is calculated to be $\sim 1200\text{\AA}$ (α is taken to be 1.7×10^5 and $0.63 \times 10^5 \text{cm}^{-1}$ for 458 and 646nm, respectively) at -0.7V vs SCE in accord with a calculation of the depletion width. In general, good agreement of PL quenching with the dead-layer model was found and a consistent set of values for α was obtained for all samples. When the experimental curves were compared to curves calculated by assuming that all of the applied potential appears in the semiconductor⁵, good accord was found, indicating that applied potential appears predominantly in the solid.

4. EL PROPERTIES

When used as a dark cathode in aqueous, $\text{OH}^-/\text{S}_2\text{O}_8^{2-}$ electrolyte, samples of $n\text{-Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$ exhibit red EL. The electrode's EL spectrum, Fig. 1, is similar to its PL spectrum, but exhibits a spectral mismatch in the high-energy tail. As with $n\text{-CdS}_x\text{Se}_{1-x}$ ($0 \leq x \leq 1$) samples, we attribute this mismatch to self-absorption effects: the enhanced intensity at short wavelengths is consistent with the origin of EL, on average, nearer the semiconductor-electrolyte interface than PL². Measured EL efficiencies are $\sim 10^{-5}$ to 10^{-6} .

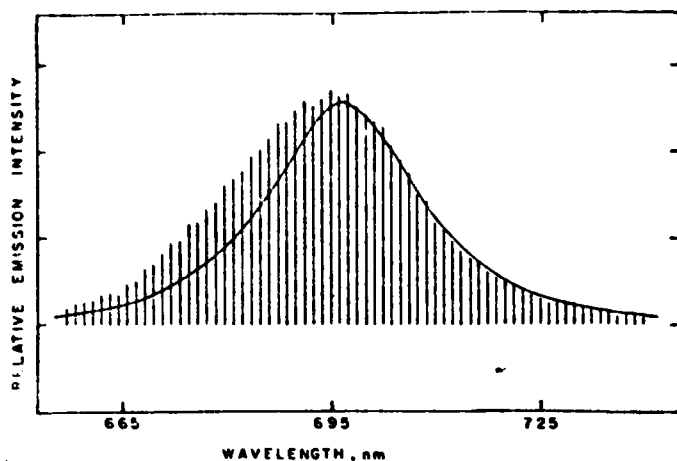
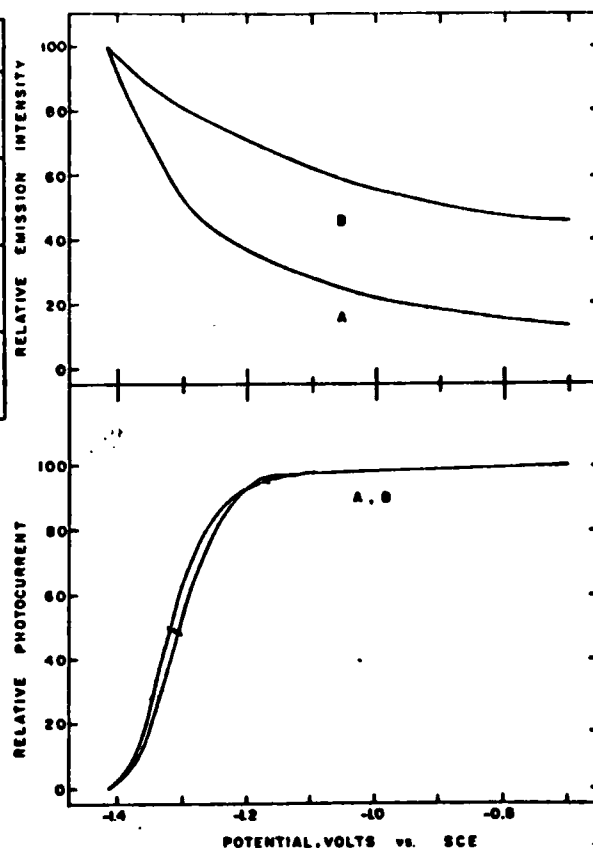


FIGURE 1

Left: Uncorrected PL (solid curve) and EL (vertical lines) spectra of $n\text{-Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$ obtained in the same sample geometry in $\text{OH}^-/\text{S}_2\text{O}_8^{2-}$ electrolyte (295K). The PL spectrum (632.8-nm excitation) was taken out of circuit; the EL spectrum, scaled to match the PL intensity at λ_{max} , was acquired by repetitively pulsing the electrode between 0.0 V (1.5 s) and -1.3 V vs. SCE (1.0 s)².

Right: Relative photocurrent (bottom panel) and PL intensity (top panel; monitored at λ_{max}) as a function of potential for an $n\text{-Cd}_{0.95}\text{Mn}_{0.05}\text{Se}$ -based PEC employing diselenide electrolyte². The electrode ($n \sim 4 \times 10^{16} \text{cm}^{-3}$) was excited with 457.9- ("A" curves) and 646-nm ("B" curves) light in an identical geometry. PL intensities and photocurrents were arbitrarily matched at "100" at open circuit; photocurrent densities (quantum yields) at -0.7 V vs. SCE are 7mA/cm^2 (0.7) and 3mA/cm^2 (0.5) for curves A and B, respectively. These i_{LV} curves were swept at 10mV/s.



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